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NOTE

Al SUBSTITUTION AND DIFFERENTIAL DISORDER IN SOIL HEMATITES

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Hematite (α-Fe_2O_3) occurs frequently in many soils developed in tropical and subtropical areas. It is usually finely divided and need be present in only small amounts to impart intense bright red coloration.

X-ray diffractograms of hematite in these soils were found to differ from reference hematites in two ways: (i) some lines are much sharper [(110), (113), (300)] than the rest and (ii) all lines show a significant shift towards lower spacings. Differential line broadening is particularly obvious when comparing the two strongest lines, of which the (104) may be more than twice as broad as the (110) line (Figure 1). The line shift to lower spacings suggests that Al replaces Fe in the hematite structure (Caillère *et al.*, 1960; Janot *et al.*, 1971; Janot and Gilbert, 1970; Perinet and Lafont, 1972b; Nahon, 1976).

In an attempt to elucidate the factors leading to these abnormal properties, hematites were synthetized in various ways, namely by heating synthetic goethite or ferrihydrite (formerly called amorphous ferric hydroxide) or by converting ferrihydrite to hematite at 70°C in aqueous suspension in the presence of Al.

As seen in Table 1 (last column), the same differential line broadening can be produced by heating synthetic goethite to 320°C. After heating to 600°C, the line broadening is significantly decreased (Francombe and Rooksby, 1959). When a 5 mole% Al substituted goethite is used, differential broadening is more pronounced at 320°C and still persists to a large extent at 600°C. Al-ferrihydrite does not convert to hematite at 320°C, but at 600°C it yields a hematite similar to the one obtained from Al-goethite.

Similar line broadening was produced with hematites synthesized from ferrihydrite in aqueous suspension at 70°C and pH 7 and 5.5 in the presence of Al, whereas without Al, a nearly normal diffractogram was obtained. With increasing amounts of Al in the system, the differential line broadening increased and both lines showed a shift towards lower spacing indicating Al substitution in the hematite structure (Gastuche *et al.*, 1964). The mole% Al substitution (Table 1) was estimated using a_0 as derived from d (110) and a linear relationship between a_0 and mole% Al based on the data of von Steinwehr (1967) and Perinet and Lafont (1972a). These data show that for hematites (prepared by heating Fe–Al-coprecipitates at >1000°C) the variation in a_0 with Al content deviates quite substantially from the Vegard rule, i.e. the simple linear interpolation between the a_0 values of hematite and corundum.

The differential line broadening has been explained for the case in which hematite forms from goethite by heating (Francombe and Rooksby, 1959). At 320°C, where the goethite has been converted to hematite, a structural subunit common to both minerals is inherited by the hematite from goethite, yielding an ordered structure in the hematite a-direction, whereas the superstructure of these sub-units in the c-direction, being different from that of goethite, is not yet fully developed. This is only achieved at 600°C, resulting in all lines being equally sharp.

In forming hematite from ferrihydrite via solution (Fischer and Schwertmann, 1975), Al seems to have a similar effect, i.e. preventing the superstructure from being attained properly, whereas the sub-units appear to be well established, although goethite is not the precursor. Since soil hematites form in the same way and since they appear to be Al substituted (Table 1) the same mechanism is believed to operate during hematite formation in soils. Al-substituted hematites showing the same differential line broadening were described from bauxites (Perinet and Lafont, 1972b).

Besides the effect of differential line broadening, small amounts of Al (5 mole%) also inhibit goethite formation under these conditions (70°C), whereas high amounts (e.g. 30 mole%) apparently lead to smaller crystals, as seen from

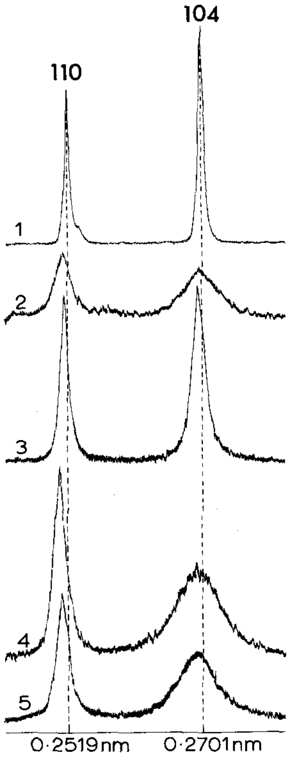

Figure 1. X-ray diffractograms of hematites from various sources: (1) natural reference (Wards); (2) natural, Oxisol, Transvaal; (3) synthetic, from ageing ferrihydrite with 5 mole% Al; (4) as before, but with 15 mole% Al; (5) synthetic, from heating 5 mole% Al goethite at 320°C.

Table 1. Properties of hematites from various sources

Source of hematite	a_0 (nm)	Al substitution (mole %)	Ratio of WHH* (104)/(110)
Natural reference (Wards)	0.5038†	0	1.0
Synthetic reference (Merck)	0.5038	0	1.0
Natural, Oxisol, Brazil	0.5020	8.2	1.9
Natural, Oxisol, Transvaal	0.5026	5.5	2.2
Synthetic, from heating goethite			
at 320°C	0.5040	0	3.0
at 600°C	0.5038	0	1.8
Synthetic, from heating Al goethite			
at 320°C	0.5024	6.4	4.0
at 600°C	0.5026	5.5	2.4
Synthetic, from heating Al ferrihydrite			
at 600°C	0.5028	4.5	2.5
Synthetic, from ageing ferrihydrite in aqueous suspension at 70°C, pH 7			
with 0 Al	0.5038	0	1.3
with 5 Al‡	0.5028	4.5	2.4
with 15 Al‡	0.5016	10.0	4.9

* Width at half height corrected for instrumental broadening using a Philips' PW 1050/70 instrument with CoKα radiation and a graphite monochromator.

† In accordance with ASTM 24-72.

‡ Al added initially to the suspension as mole% of Fe + Al.

a general increase in the line broadening, until Al finally inhibits any crystallization (Gastuche *et al.*, 1964), depending on such factors as the pH and temperature of the system (details to be published elsewhere).

Preliminary results show that Ti coprecipitated with Fe as ferrihydrite also seems to enhance the differential line broadening of resulting hematite, although to a lesser extent than Al.

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REFERENCES

Caillère, S., Gatineau, L. and Hénin, St. (1960) Préparation à basse température d'hématite alumineuse: *Compt. Rend.* **250**, 3677–3679.

Fischer, W. R. and Schwertmann, U. (1975) The formation of hematite from amorphous iron(III) hydroxide: *Clays and Clay Minerals* **23**, 33–37.

Francombe, M. H. and Rooksby, H. P. (1959) Structure transformations effected by the dehydration of diaspore, goethite and delta ferric oxide: *Clay Minerals Bull.* **4**, 1–14.

Gastuche, M. C., Bruggenwert, T. and Mortland, M. M. (1964) Crystallization of mixed iron and aluminium gels: *Soil Sci.* **98**, 281–289.

Janot, C. and Gilbert, H. (1970) Les constituants du fer dans certaines bauxites naturelles étudiées par effet Mössbauer: *Bull. Soc. Franç. Minér. Crist.* **93**, 213–223.

Janot, C., Gibert, H., Grammont, X. De Gramont and Bias R. (1971) Étude des substitutions Al–Fe dans les roches latéritiques: *Bull. Soc. Franç. Minér. Crist.* **94**, 367–380.

Nahon, D. (1976) Cuirasses ferrigineuses et encroûtment calcaires ou Senegal occidental et en Mauritanie: Thése, Université de Marseille, 232 pp.

Perinet, G. and Lafont, R. (1972a) Sur le paramètres cristallographiques des hèmatites alumineuses: *Compt. Rend.* **275**, 1021–1024.

Perinet, G. and Lafont, R. (1972b) Sur la présence d'hématite alumineuse désordonée dans des bauxites du Var: *Compt. Rend.* **274**, 272–274.

von Steinwehr, H. E. (1967) Gitterkonstanten im System α-(Al, Fe, Cr)$_2$O$_3$ und ihr Abweichen von der Vegardregel: *Z. Krist.* **125**, 377–403.

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